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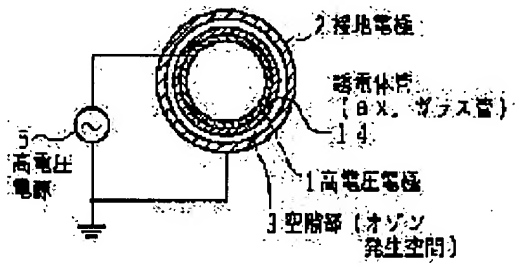
(54) HIGH-VOLTAGE ELECTRODE STRUCTURE OF OZONE GENERATOR

(57)Abstract:

PURPOSE: To improve corrosion resistance without impairing adhesion to a dielectric tube by forming a high-voltage electrode by flame-spraying aluminum coat to dielectrics provided with the high-pressure electrode and forming Ni-Cr coat on this electrode.

CONSTITUTION: In a silent discharge type ozone generator provided with a dielectric substance in which high-voltage electrode 1 is provided and a ground electrode 2 arranged oppositely to this dielectric substance through a space part 3 and capable of generating ozone in a raw material gas communicating into the space part 3 by applying voltage between the high-voltage electrode 1 and the ground electrode 2, this high-voltage electrode structure is formed as follows.



(1) Aluminum coat is flame-sprayed to the above dielectric substance to form a high voltage electrode 1 and Ni-Cr coat is formed on this high-voltage electrode by prescribed means (e.g. flame spraying) or

(2) aluminum coat is flame-sprayed to the above dielectric substance to form the high-voltage electrode 1 and a chromium coat is formed on this high-voltage electrode 1 by prescribed means (e.g. metal plating).

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the high-voltage electrode structure of the silent discharge-type ozone generator used for water treatment, treatment of human waste, etc.
[0002]
[Description of the Prior Art] Ozone has very strong oxidizing power and is used for many applications, such as sterilization in vertical water treatment, treatment of human waste, and food relation, such as sterilization of water, deordorization, and decolorization. Although there are a UV irradiation method, a radiation irradiation method, a plasma electric discharge method, a silent discharge method, an electrolysis-of-water method, etc. as method of generating ozone, a silent discharge method is a subject industrially. The principle of the ozone generator by the silent discharge method is shown in drawing 2 . In drawing 2 , the high-voltage electrode 1 and an earth electrode 2 make a dielectric 4 intervene, and are installed so that the opening section 3 may be formed among both. Ozone is generated by letting two electrodes 1 and the gas (dry air or oxygen) which impresses for example, AC electrical potential difference among two, is made to generate silent discharge in the opening section 3, and serves as a raw material pass in this opening section 3.
[0003] The theoretical yield of ozone O3 is O2 ->O+O-118Kcal (endothermic reaction).
O+O2 ->O3+25Kcal (exothermic reaction)
More, it is set to 3O2 ->2O3-68Kcal, and 34 Kcals are needed in order to generate O3 [one-mol]. Therefore, theoretical yield is set to 1.2kgO(s)3/kWh. However, the present condition of an ozone generator is not passing over the generation effectiveness of ozone over power consumption to several% very low compared with a theoretical yield, but about ninety% of remaining power's serving as heat, and having not contributed to ozone generation.
[0004]
[Problem(s) to be Solved by the Invention] As main factors which affect the amount of generation of ozone, the wave of the configuration of an electrode, the magnitude of an inter-electrode gap, the configuration of a dielectric and the quality of the material, the cooling approach of an electrode, dehumidification and the cooling approach of material gas, and applied voltage etc. is mentioned.
[0005] The present ozone generator has the main structure of applying the silent discharge which

makes a dielectric intervening so that an opening may be formed in inter-electrode, and makes discharge causing in the opening part etc., as drawing 2 showed. In order to generate stable silent discharge, while setting inter-electrode gap length to several mm or less, it is necessary to make gap length into homogeneity, and it is necessary to generate discharge uniformly in a gap part. An example of the structure of the electrode section of an actual ozone generator is shown in drawing 1 .

[0006] In drawing 1 , (a) shows the cross section of the discharge tube and (b) shows the structure of dielectric tubing. 14 is dielectric tubing of the cylinder with which the end was blockaded and the other end was released, for example, has structure with the glass tube. The high-voltage electrode 1 is formed in the internal surface of the dielectric tubing 14. The earth electrode 2 is installed in the concentric circle periphery of the dielectric tubing 14 side by side through the opening section (silent discharge section) 3. 5 is a high-voltage power source which impresses the predetermined high voltage between the high-voltage electrode 1 and an earth electrode 2.

[0007] In the structure of drawing 1 , the dependability of the high-voltage electrode 1 which prepares discharge inside the dielectric tubing 14 used as a high voltage electrode stability and in order to make it generate uniformly becomes important. The coating which carbon generally mixed is applied to high-voltage electrode layer production of the ozone discharge tube like drawing 1 , or the approach which has ****ed thermal spraying of the aluminum powder enough, and carries out it is used for it.

[0008] When the raw material air gas which dried these electrode coats touches, it is satisfactory, but if the damp open air is contacted, degradation of an electrode coat will take place. namely, nitrogen content child N2* (active species) excited by discharge from the nitrogen content child N2 -- generating -- N2 -- O and NO -- nitrogen oxides, such as ....., are generated. Also in it, N 2O5 will react with the moisture in the damp open air which invades when it becomes a liquid and the door of a tank is opened at the time of the shutdown of equipment, and will be able to do a nitric acid. If this nitric acid adheres to the thermal-spraying coat electrode of aluminum, aluminum will be corroded, degradation of a high-voltage electrode coat will take place, and there is a trouble that the glass discharge tube will finally result in destruction.

[0009] The purpose is in offering the high-voltage electrode structure of an ozone generator excellent in corrosion resistance by having made this invention in view of the above-mentioned point, without spoiling adhesion with dielectric tubing.

[0010]

[Means for Solving the Problem] This invention equips the dielectric with which the high-voltage electrode was prepared, and this dielectric with the earth electrode by which opposite arrangement was carried out through the opening section. In the silent discharge-type ozone generator which generates ozone in the material gas which the electrical potential difference was impressed [material gas] to said high-voltage electrode and touch-down inter-electrode, and circulated said opening circles (1) After carrying out thermal spraying of the aluminum coat to said dielectric and forming a high-voltage electrode, It is characterized by forming a nickel-Cr coat with a predetermined means (for example, thermal spraying) on this high-voltage electrode. (2) After carrying out thermal spraying of the aluminum coat to said dielectric and forming a high-voltage electrode, it is characterized by

forming a chromium coat with a predetermined means (for example, plating processing) on this high-voltage electrode.
[0011]
[Function]
(1) Since the nickel-Cr coat is formed on a high-voltage electrode, the aluminum thermal-spraying coat with sufficient adhesion with the glass tube used for a dielectric does not contact a direct nitric acid. nickel-Cr is excellent in corrosion resistance, such as ozone resistance and nitric-acid-proof nature. For this reason, the high-voltage electrode excellent in corrosion resistance can be formed, holding adhesion with a dielectric with an aluminum thermal-spraying coat.
[0012] (2) Since the chromium coat is formed on a high-voltage electrode, the aluminum thermal-spraying coat with sufficient adhesion with the glass tube used for a dielectric does not contact a direct nitric acid. Chromium is excellent in corrosion resistance, such as ozone resistance and nitric-acid-proof nature. For this reason, the high-voltage electrode excellent in corrosion resistance can be formed, holding adhesion with a dielectric with an aluminum thermal-spraying coat.
[0013]
[Example] One example of this invention is explained referring to a drawing below. In this invention, in order to solve the above-mentioned trouble, the structure where an aluminum thermal-spraying coat with sufficient adhesion with the glass tube used for a dielectric did not contact a direct nitric acid was adopted.
[0014] That is, by invention of a publication, thermal spraying is carried out to claims 1 and 2 from the high-voltage electrode 1 of the aluminum thermal-spraying coat which shows nickel-Cr excellent in corrosion resistance, such as ozone resistance and nitric-acid-proof nature, to drawing 1 (b). The spray condition of nickel-Cr is as follows.
[0015] Particle size distribution of a nickel-Cr particle -- Thermal-spraying thickness of 44-micrometeror less nickel-Cr -- The high-voltage electrode excellent also in corrosion resistance could be formed with the nickel-Cr thermal-spraying coat, this holding about 50 micrometers of adhesion with the glass tube of a substrate with an aluminum thermal-spraying coat. In addition, when thermal spraying of nickel-Cr is carried out to direct glass, the adhesion of a coat is not so good as aluminum.
[0016] Moreover, in invention given in claims 3 and 4, plating processing is carried out from the high-voltage electrode 1 of the aluminum thermal-spraying coat which shows chromium excellent in corrosion resistance, such as ozone resistance and nitric-acid-proof nature, to drawing 1 (b). The plating processing conditions of chromium are as follows.
[0017] Etchant [The high-voltage electrode excellent also in corrosion resistance could be formed with the chrome plating coat, holding adhesion with the glass tube of a substrate with an aluminum thermal-spraying coat by this three to 4 min.] -- Chromic anhydride 250 g/l, sulfuric-acid 1.5 g/l, **** fluoric acid 5 g/l bath temperature -- 50-degree-C current density -- 50 A/dm2 plating time amount
[0018]
[Effect of the Invention] Since the nickel-Cr coat was formed by thermal spraying on this high-voltage electrode according to invention given in claims 1 and 2 as mentioned above after carrying out thermal spraying of the aluminum coat to the dielectric and forming a high-voltage electrode, the

following outstanding effectiveness is acquired.
(1) By giving a nickel-Cr thermal-spraying coat on the conventional aluminum thermal-spraying coat electrode, corrosion resistance, such as ozone resistance and nitric-acid-proof nature, was able to be improved.
[0019] Moreover, since according to invention given in claims 3 and 4 the chromium coat was formed by plating processing on this high-voltage electrode after carrying out thermal spraying of the aluminum coat to the dielectric and forming a high-voltage electrode, the following outstanding effectiveness is acquired.
(2) By performing chrome plating processing on the conventional aluminum thermal-spraying coat electrode, corrosion resistance, such as ozone resistance and nitric-acid-proof nature, was able to be improved.
[0020] Furthermore, according to invention given in claims 1, 2, 3, and 4, the following outstanding effectiveness is acquired.
(3) The high-voltage electrode of this invention and dielectric tubing (for example, glass tube) of a substrate touch by the aluminum thermal-spraying film, and its adhesion is good. The discharge electrode excellent also in corrosion resistance for ozone generating could be manufactured without spoiling this adhesion.
(4) Since the dependability of the high voltage electrode section of dielectric tubing improved, a mass ozone generator can be operated safely and ozonization gas could be supplied to stability.

[Translation done.]

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CLAIMS

[Claim(s)]
[Claim 1] The dielectric with which the high-voltage electrode was prepared, and this dielectric are equipped with the earth electrode by which opposite arrangement was carried out through the opening section. In the silent discharge-type ozone generator which generates ozone in the material gas which the electrical potential difference was impressed [material gas] to said high-voltage electrode and touch-down inter-electrode, and circulated said opening circles High-voltage electrode structure of the ozone generator characterized by forming a nickel-Cr coat with a predetermined means on this high-voltage electrode after carrying out thermal spraying of the aluminum coat to said dielectric and forming a high-voltage electrode.
[Claim 2] Said predetermined means is the high-voltage electrode structure of the ozone generator according to claim 1 characterized by being what depended on thermal spraying.
[Claim 3] The dielectric with which the high-voltage electrode was prepared, and this dielectric are equipped with the earth electrode by which opposite arrangement was carried out through the opening section. In the silent discharge-type ozone generator which generates ozone in the material gas which the electrical potential difference was impressed [material gas] to said high-voltage electrode and touch-down inter-electrode, and circulated said opening circles High-voltage electrode structure of the ozone generator characterized by forming a chromium coat with a predetermined means on this high-voltage electrode after carrying out thermal spraying of the aluminum coat to said dielectric and forming a high-voltage electrode.
[Claim 4] Said predetermined means is the high-voltage electrode structure of the ozone generator according to claim 3 characterized by being what depended on plating processing.

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JAPANESE [JP,07-002501,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS OPERATION EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The outline of the discharge tube used with the ozone generator of this invention is shown, for (a), it is a discharge tube sectional view and (b) is dielectric tubing structural drawing.
[Drawing 2] The explanatory view showing the principle of the ozone generation by the silent discharge method.

[Description of Notations]
1 -- High-voltage electrode
2 -- Earth electrode
3 -- Opening section
4 -- Dielectric
5 -- High-voltage power source
14 -- Dielectric tubing

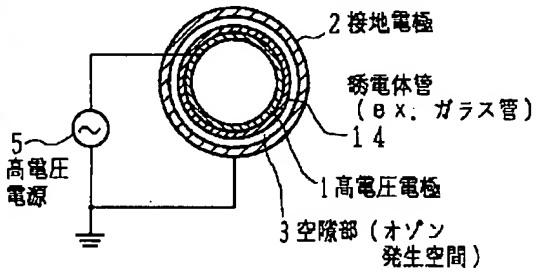
[Translation done.]

Drawing selection

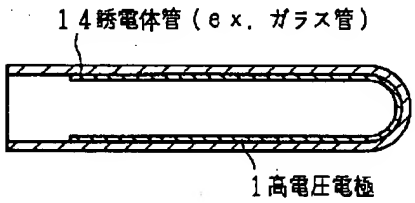
Representative drawing

オゾン発生用放電管の概略図

(a) 放電管断面



(b) 誘電体管構造



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Ｃ０１Ｂ　13/11		Ｇ		

審査請求　未請求　請求項の数４　ＯＬ　（全４頁）

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(22)出願日　平成５年(1993)７月９日
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(32)優先日　平５(1993)４月23日
(33)優先権主張国　日本（ＪＰ）

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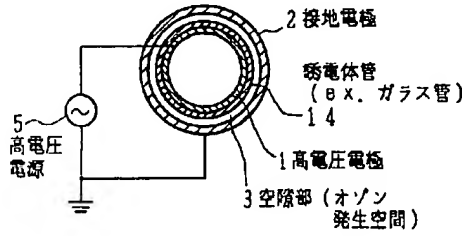
(54)【発明の名称】　オゾン発生装置の高電圧電極構造

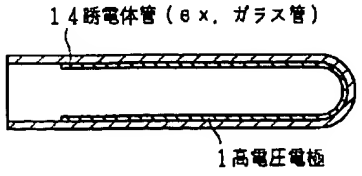
(57)【要約】
【目的】　高電圧電極１が設けられた誘電体管１４と、該誘電体管１４に空隙部３を介して対向配設された接地電極２とを備え、前記高電圧電極１と接地電極２間に電圧を印加して前記空隙部３内に流通させた原料ガス中にオゾンを発生させる無声放電式のオゾン発生装置において、誘電体管１４との密着性を損なうことなく耐腐食性に優れた高電圧電極構造を提供する。
【構成】　前記誘電体管１４にアルミ被膜を溶射して高電圧電極１を形成した後、該高電圧電極１上にＮｉ－Ｃｒを溶射する。高電圧電極１上にＮｉ－Ｃｒ被膜を形成しているので、該電極１は、空隙部３において水分と反応して発生した硝酸と接触することはない。

オゾン発生用放電管の概略図

（ａ）放電管断面



（ｂ）誘電体管構造



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【特許請求の範囲】

【請求項１】　高電圧電極が設けられた誘電体と、該誘電体に空隙部を介して対向配設された接地電極とを備え、前記高電圧電極と接地電極間に電圧を印加して前記空隙部内に流通させた原料ガス中にオゾンを発生させる無声放電式のオゾン発生装置において、

前記誘電体にアルミ被膜を溶射して高電圧電極を形成した後、該高電圧電極上にＮｉ－Ｃｒ被膜を所定の手段によって形成したことを特徴とするオゾン発生装置の高電圧電極構造。

【請求項２】　前記所定の手段は溶射によるものであることを特徴とする請求項１に記載のオゾン発生装置の高電圧電極構造。

【請求項３】　高電圧電極が設けられた誘電体と、該誘電体に空隙部を介して対向配設された接地電極とを備え、前記高電圧電極と接地電極間に電圧を印加して前記空隙部内に流通させた原料ガス中にオゾンを発生させる無声放電式のオゾン発生装置において、

前記誘電体にアルミ被膜を溶射して高電圧電極を形成した後、該高電圧電極上にクロム被膜を所定の手段によって形成したことを特徴とするオゾン発生装置の高電圧電極構造。

【請求項４】　前記所定の手段はメッキ処理によるものであることを特徴とする請求項３に記載のオゾン発生装置の高電圧電極構造。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、水処理や屎尿処理等に利用される無声放電式のオゾン発生装置の高電圧電極構造に関する。

【０００２】

【従来の技術】オゾンは極めて強い酸化力を有し、水の殺菌、脱臭、脱色等の上下水処理や屎尿処理及び食品関連における殺菌などの多くの用途に使われている。オゾンの生成法には、紫外線照射法、放射線照射法、プラズマ放電法、無声放電法及び水の電気分解法等があるが、工業的には無声放電法が主体である。図２に無声放電法によるオゾン発生装置の原理を示す。図２において高電圧電極１と接地電極２は、両者間に空隙部３が形成されるように誘電体４を介在させて並設されている。両電極１，２間に例えばＡＣ電圧を印加して空隙部３で無声放電を発生させ原料となるガス（乾燥空気もしくは酸素）をこの空隙部３に通すことによりオゾンを発生させている。

【０００３】オゾンO_3の理論収率は、

$O_2 \rightarrow O + O - 118Kcal$（吸熱反応）

$O + O_2 \rightarrow O_3 + 25Kcal$（発熱反応）

より、

$3O_2 \rightarrow 2O_3 - 68Kcal$

となり、O_3を１ｍｏｌ生成するために３４Ｋｃａｌ必

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要となる。従って理論上の収率は１．２ｋｇO_3／ＫＷｈとなる。しかし、消費電力に対するオゾンの生成効率は理論収率に比べて極めて低く数％に過ぎず、残りの９０数％の電力は熱となってオゾン生成に寄与していないというのがオゾン発生装置の現状である。

【０００４】

【発明が解決しようとする課題】オゾンの生成量に影響を及ぼす主な因子としては、電極の形状、電極間ギャップの大きさ、誘電体の形状及び材質、電極の冷却方法、原料ガスの除湿や冷却方法、印加電圧の波形等が挙げられる。

【０００５】現在のオゾン発生装置は図２で示したように、電極間に空隙が形成されるように誘電体を介在させて、その空隙部分で放電を起こさせる無声放電を応用する構造などが主となっている。安定な無声放電を発生させるためには電極間ギャップ長を数ｍｍ以下にするとともにギャップ長を均一にして、放電をギャップ部分で一様に発生させる必要がある。実際のオゾン発生装置の電極部分の構造の一例を図１に示す。

【０００６】図１において（ａ）は放電管の断面、（ｂ）は誘電体管の構造を示している。１４は一端が閉塞され他端が解放された円筒の誘電体管であり、例えばガラス管で構造されている。誘電体管１４の内壁面には高電圧電極１が設けられている。誘電体管１４の同心円外周には空隙部（無声放電部）３を介して接地電極２が並設されている。５は高電圧電極１と接地電極２の間に所定の高電圧を印加する高電圧電源である。

【０００７】図１の構造において、放電を安定且つ一様に発生させるためには、高圧電極となる誘電体管１４の内側に設ける高電圧電極１の信頼性が重要となる。図１のようなオゾン放電管の高電圧電極膜作製には、一般にカーボンの混入した塗料を塗布したり、アルミ粉末を溶射したりする方法が用いられている。

【０００８】これらの電極被膜は乾燥した原料空気ガスが接触している時は問題はないが、湿った外気と接触すると、電極被膜の劣化が起こる。すなわち放電によって窒素分子N_2から励起された窒素分子N_2＊（活性種）が発生し、N_2O，ＮＯ……などの窒素酸化物が生成される。その中でもN_2O_5は液体となり、装置の運転停止時にタンクの扉を開けたときなどに侵入してくる湿った外気の中の水分と反応して硝酸ができてしまう。この硝酸がアルミの溶射被膜電極に付着するとアルミが腐食されて高電圧電極被膜の劣化が起こり、最終的にガラス放電管が破壊に至ってしまうという問題点がある。

【０００９】本発明は上記の点に鑑みてなされたものでその目的は、誘電体管との密着性を損なうことなく耐腐食性に優れたオゾン発生装置の高電圧電極構造を提供することにある。

【００１０】

【課題を解決するための手段】本発明は、高電圧電極が

設けられた誘電体と、該誘電体に空隙部を介して対向配設された接地電極とを備え、前記高電圧電極と接地電極間に電圧を印加して前記空隙部内に流通させた原料ガス中にオゾンを発生させる無声放電式のオゾン発生装置において、（1）前記誘電体にアルミ被膜を溶射して高電圧電極を形成した後、該高電圧電極上にＮｉ－Ｃｒ被膜を所定の手段（例えば溶射）によって形成したことを特徴とし、（2）前記誘電体にアルミ被膜を溶射して高電圧電極を形成した後、該高電圧電極上にクロム被膜を所定の手段（例えばメッキ処理）によって形成したことを特徴としている。

【0011】

【作用】

（1）高電圧電極上にＮｉ－Ｃｒ被膜を形成しているので、誘電体に用いられるガラス管との密着性が良いアルミ溶射被膜は直接硝酸と接触することはない。Ｎｉ－Ｃｒは耐オゾン性や耐硝酸性などの耐腐食性に優れている。このため誘電体との密着性をアルミ溶射被膜で保持しつつ、耐腐食性に優れた高電圧電極を形成することができる。

【0012】（2）高電圧電極上にクロム被膜を形成しているので、誘電体に用いられるガラス管との密着性が良いアルミ溶射被膜は直接硝酸と接触することはない。クロムは耐オゾン性や耐硝酸性などの耐腐食性に優れている。このため誘電体との密着性をアルミ溶射被膜で保持しつつ、耐腐食性に優れた高電圧電極を形成することができる。

【0013】

【実施例】以下図面を参照しながら本発明の一実施例を説明する。本発明では前述の問題点を解決するために誘電体に用いられるガラス管との密着性が良いアルミ溶射被膜が直接硝酸と接触しないような構造を採用した。

【0014】すなわち請求項1、2に記載の発明では、耐オゾン性や耐硝酸性などの耐腐食性に優れたＮｉ－Ｃｒを図1（ｂ）に示すアルミ溶射被膜の高電圧電極1の上から溶射する。Ｎｉ－Ｃｒの溶射条件は次のとおりである。

【0015】Ｎｉ－Ｃｒ粒子の粒度分布…４４μｍ以下
Ｎｉ－Ｃｒの溶射厚さ…５０μｍ程度
これにより下地のガラス管との密着性をアルミ溶射被膜で保持しつつ、Ｎｉ－Ｃｒ溶射被膜により、耐腐食性にも優れた高電圧電極を形成することができるようになった。尚Ｎｉ－Ｃｒを直接ガラスに溶射した場合、アルミほど被膜の密着性は良くない。

【0016】また請求項3、4に記載の発明では、耐オゾン性や耐硝酸性などの耐腐食性に優れたクロムを図1（ｂ）に示すアルミ溶射被膜の高電圧電極1の上からメッキ処理する。クロムのメッキ処理条件は次のとおりである。

【0017】エッチャント…無水クロム酸２５０ｇ／ｌ、硫酸１．５ｇ／ｌ、けいふっ酸５ｇ／ｌ
浴温…５０℃
電流密度…５０Ａ／ｄｍ²
めっき時間　3～4ｍｉｎ
これにより下地のガラス管との密着性をアルミ溶射被膜で保持しつつ、クロムメッキ被膜により、耐腐食性にも優れた高電圧電極を形成することができるようになった。

【0018】

【発明の効果】以上のように請求項1、2に記載の発明によれば、誘電体にアルミ被膜を溶射して高電圧電極を形成した後、該高電圧電極上にＮｉ－Ｃｒ被膜を溶射によって形成したので、次のような優れた効果が得られる。

（1）従来のアルミ溶射被膜電極上にＮｉ－Ｃｒ溶射被膜を施すことにより、耐オゾン性や耐硝酸性などの耐腐食性を向上することができた。

【0019】また請求項3、4に記載の発明によれば、誘電体にアルミ被膜を溶射して高電圧電極を形成した後、該高電圧電極上にクロム被膜をメッキ処理によって形成したので、次のような優れた効果が得られる。

（2）従来のアルミ溶射被膜電極上にクロムメッキ処理を施すことにより、耐オゾン性や耐硝酸性などの耐腐食性を向上することができた。

【0020】さらに請求項1、2、3、4に記載の発明によれば次のような優れた効果が得られる。

（3）本発明の高電圧電極と下地の誘電体管（例えばガラス管）とはアルミ溶射膜で接触しており、密着性が良い。この密着性を損なうことなく、耐腐食性にも優れたオゾン発生用の放電電極を製作できるようになった。

（4）誘電体管の高圧電極部の信頼性が向上したため、大容量のオゾン発生装置を安全に運転でき、オゾン化ガスを安定に供給することができるようになった。

【図面の簡単な説明】

【図1】本発明のオゾン発生装置で用いる放電管の概略を示し、（ａ）は放電管断面図、（ｂ）は誘電体管構造図。

【図2】無声放電法によるオゾン生成の原理を示す説明図。

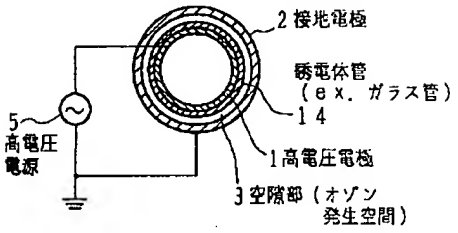
【符号の説明】

1…高電圧電極
2…接地電極
3…空隙部
4…誘電体
5…高電圧電源
１４…誘電体管

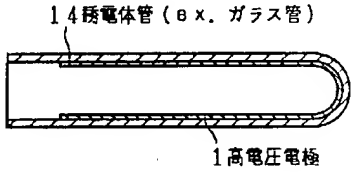
【図１】

オゾン発生用放電管の概略図

（ａ）放電管断面



（ｂ）誘電体管構造



【図２】

無声放電法によるオゾン生成の原理図